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Title: ATOMIC INTERACTIONS BETWEEN PLUTONIUM AND HELIUM

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Atomic Interactions Between Plutonium and Helium

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Abstract

An essential issue in gallium (Ga) -stabilized fcc-phase plutonium (δ-Pu) is the formation of helium (He) voids and bubbles emanating from the radiolytic decay of the Pu. The rate of formation of He voids and bubbles is related to the He-defect formation energies and their associated migration barriers. The size and shape distributions of the bubbles are coupled to these critical migration processes. The values of the defect formation energies, internal pressure, and migration barriers can be estimated from atomistic calculations. Complicating this picture is the destruction of He-filled voids and bubbles by subsequent radiolytic decay events.

The present study concerns the construction of the necessary potential energy surfaces for the Pu-He and He-He interactions within the modified embedded atom method (MEAM) [1-4]. Once fully tested, the potentials will be used to estimate the He-defect formation energies and barriers to the migration of these defects for both interstitial and substitutional He on an *fcc* Pu lattice.

The He-He interactions are modeled from *ab initio* electronic structure calculations for the He_2 dimer and the equilateral He_3 trimer [5-6]. The experimental data and the electronic structure calculations on He_2 agree very well. (See Fig. 1.) These data were fit to a Rose function [1-3], $f_R(x) = A\,P(\alpha x)\exp(-\alpha x)$, where P is a polynomial, $x = R/R_0-1$, R is the bond length, and R_0 is its equilibrium value. The fits are

very satisfactory. Both linear ($P = 1+\alpha x$, zeroth-order Rose) and rational ($P = 1+\alpha x+a_3 (\alpha x)^3/(1+x)$, first-order Rose) polynomials in the Rose function were tried. The more flexible rational form does improve the fit, but only marginally. Only the linear form was used thereafter. The resulting MEAM potential was used to predict the behavior of the linear trimer [7] and the *fcc* cold compression curve [8]. The results are shown in Fig. 2 and appear to be satisfactory.

The compression regions of the curves are of particular interest for several reasons. First, an octahedral interstitial He atom in an *fcc* Pu lattice with a lattice constant of 4.64 Å has a nearest Pu neighbor distance of 2.32 Å. This distance is in the compressive region of the potential energy curve. Second, the compressive region will partially determine the internal pressure of He-filled voids and bubbles. Third, the shape of the He-filled voids will be influenced by the compression region of the potential.

The Pu-He interactions are also modeled from *ab initio* electronic structure calculations, this time only for the PuHe dimer [9]. The lowest-energy spin state of the dimer appears to be the S=7/2 state with a "Stuttgart small-core RECP/6-31g" basis. Two electronic structure methods were tried which would bound the extremes of the Pu-He interaction. One was the local density approximation (LDA) [10], which tends to overestimate binding strength. It gives a well depth of 0.08 eV and a bond length of 3.6 Å. The other used the Becke-3-Lee-Yang-Parr (B3LYP) exchange-correlation energy functional [11], which tends to underestimate binding strength. It predicts no binding at any separation. For purposes of fitting to the Rose functional form, a well depth of 0.03 eV and bond length of 4.8 Å was used. The bond length exceeds the cutoff distance that will be used in future simulations to limit the maximum range of the atomic interactions and is effectively purely repulsive.

Furthermore, the dimer information is sufficient to determine the pairwise part of the Pu-He MEAM potential, but not the effective electron density that determines the many-body part of the potential, the

embedding functions F_{He} and F_{Pu} in Fig. 3. The effective electron density, as well as determining which of the two dimer curves (LDA or B3LYP) is preferable, will be decided by comparing simulation results to known information about He bubble formation rates at elevated temperatures and estimates of He bubble sizes. Initial simulations suggest that an interstitial He defect, based on either the LDA or the B3LYP dimer curve with a He:Pu density ratio of 0.04, will not remain at an octahedral site as in other fcc metals such as nickel. The He defect may also form a split interstitial with a Pu atom. The details remain to be determined.

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Fig. 1. Electronic structure, experimental, and fit energies for He_2.

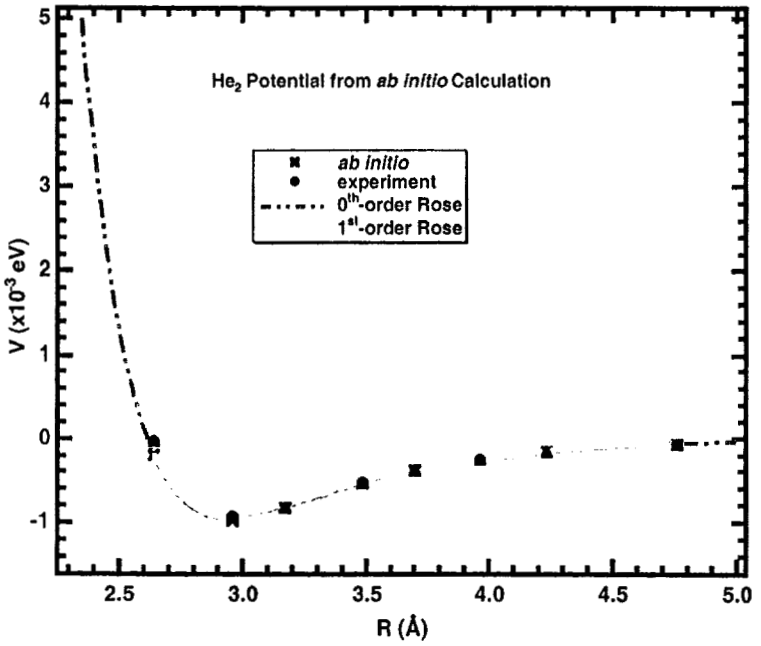

Fig. 2. Experimental energies and fits for He_2, *ab initio* electronic structure energies and fits for both equilateral and linear He_3, and cold compression curve for *fcc* He.

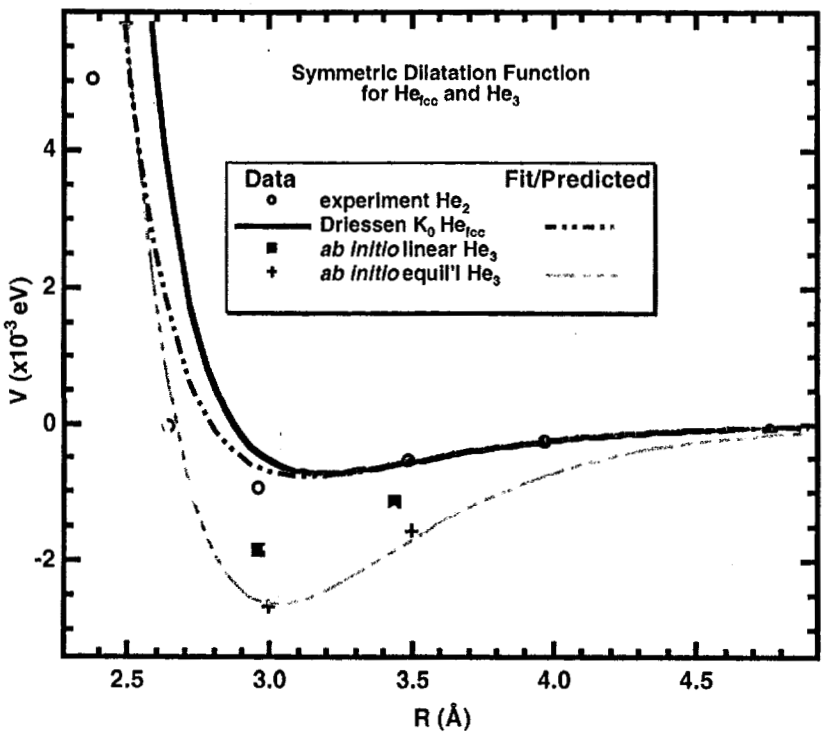

Fig. 3. *Ab initio* electronic structure energies and fits for PuHe from LDA electronic structure method and the energy components of the MEAM dimer potential. The components are computed with a He-Pu density ratio of 0.04 at the He-HE bond length of 2.96 Å.